OBSERVATIONS ON THE RARE EARTHS: SEPARATION OF THE YTTRIUM EARTHS

BY

HOWARD EARL KREMERS

A.B., Western Reserve University, 1939

M.S., Syracuse University, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1944

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OBSERVATIONS ON THE RARE EARTHS: SEPARATION OF THE YTTRIUM EARTHS

I. DOUBLE SODIUM SULFATE PRECIPITATION FOR THE SEPARATION OF YTTRIUM AND THE TERBIUM AND YTTRIUM EARTHS.

Since there was no reliable information on the use of double sodium rare earth sulfate precipitation as a fractionation procedure to separate the terbium and yttrium group elements, experiments were performed to show the utility of this method for the separation of these earths.

Crude rare earth oxides containing about five per cent yttrium earths were treated in nitrate solution with powdered sodium sulfate until most of the cerium earths had precipitated. The mother liquor was fractionated by systematic double sulfate precipitation in series of three to five fractions until sixty-five fractionations had been made. The fractionation was controlled by spectrophotometric analyses[1] and by average atomic weight determinations.

There was no appreciable difference in efficiency when the fractionations were performed in hot or cold solutions, although precipitation from hot solutions was more convenient. In the fractionation, it was found convenient to precipitate about one-third of the rare earths at room temperature, and then to warm the mother earth to obtain a second precipitate and mother liquor.

There was no sharp separation of the cerium, terbium and yttrium groups. The cerium earths of lower atomic number concentrated rapidly in the soluble fractions, the terbium earths and cerium earths of higher atomic number concentrated in the intermediate fractions, and the yttrium earths concentrated with yttrium in the soluble fractions. There was a tendency for the cerium earths of higher atomic number to remain in the more soluble fractions.

After two precipitations at room temperature and two precipitations from hot solutions, the initial crude rare earths gave oxides from the mother liquor containing more than ninety-five per cent yttrium earths. Erbium, holmium, and to a lesser extent dysprosium, concentrated with yttrium in the fractionation. There was no appreciable separation of erbium from holmium.

The experiments showed that double sodium rare earth sulfate precipitation serves only for the isolation of groups of rare earth elements which must be fractionated by other means to effect a complete resolution.

II. PREPARATION OF RARE EARTH BROMATES FROM RARE EARTH PERCHLORATES.

The disadvantage of the usual preparation of rare earth bromates by methathesis between rare earth sulfates and barium bromate is that the barium sulfate precipitate occludes rare earths. A study was undertaken to determine if rare earth bromates suitable for fractionation could be prepared by metathesis between rare earth perchlorate and potassium bromate. The slightly soluble potassium perchlorate thereby precipitated would have less tendency to occlude rare earths than would barium sulfate.

Powdered potassium bromate was added to boiling yttrium earth perchlorate solutions, and after cooling, the potassium perchlorate precipitate was removed by filtration. This precipitate contained insignificant amounts of rare earths. The filtrates were fractionally crystallized until six fractions were obtained, and the fractions were then analyzed.

Potassium bromate and potassium perchlorate rapidly concentrated in the insoluble fractions, and small amounts of rare earth perchlorates concentrated in the soluble fractions.

The preparation of rare earth bromates from rare earth perchlorates is more convenient than the preparation from rare earth sulfates, but the removal of the reaction by-products is not complete with the perchlorate method. This objection is not important because most of the by-products can be removed during fractionation.

III. BASICITY SEPARATIONS OF THE RARE EARTHS.

AN ELECTROMETRIC STUDY OF THE PRECIPITATION OF HYDROUS TRIVALENT RARE EARTH HYDROXIDES

Although the order of relative basicity of rare earth compounds has been studied by various basicity separation methods, there is no complete tabulation of the basicity order as determined by the comparison of individual rare earth compounds under similar conditions. Electrometric titrations of rare earth nitrate, sulfate and acetate solutions with sodium hydroxide were made to determine the relative basicities and solubilities of rare earth hydroxides. The trivalent rare earths studied (lanthanum, cerium, praseodymium, neodymium, samarium, europium gadolinium, yttrium, erbium, thulium, ytterbium and lutecium) were of the best quality on hand.

The titration data showed that the basicity of the lanthanides which were studied decreases with increase in atomic number, with yttrium falling between gadolinium and erbium. The *p*H values during precipitation showed that the coordinating ability of the rare earths increases with decrease in basicity and that the acetate ion coordinates more rapidly with rare earth ions than do sulfate or nitrate ions. The nitrate ion showed the least coordination tendency. The slowness with which equilibrium was established during precipitation indicated that oxolation is an important factor in the coagulation of rare earth hydroxides.

Values for solubility product constants for the rare earth hydroxides were determined. These values agree satisfactorily with reported values. The *p*H of precipitation of the rare earth hydroxides was determined for precipitation from nitrate, sulfate, and acetate solutions. These values showed that in basicity separations, nitrates are to be preferred for the cerium earths, acetates are to be preferred for the terbium earths, and sulfates are to be recommended for the yttrium earths.

FRACTIONAL PRECIPITATION OF THE YTTRIUM EARTHS WITH UREA

Fogg and Hess[2] showed that the hydrolysis of urea in hot aqueous solutions to give ammonia could be utilized as a method for basicity fractionations of the yttrium earths. The success of this method was verified.

Several yttrium earth materials were fractionated by the urea method. The fractionation showed that the method compares favorably with the basic nitrite and basic nitrate methods, but it is not as efficient as the ferrocyanide method for the separation of erbium from yttrium.

The urea method is not as convenient to use as the basic nitrite method because long periods of heating are required with the urea method to obtain good yields of precipitates.

IV. SEPARATION OF ERBIUM FROM YTTRIUM BY FRACTIONAL PRECIPITATION OF THE FERROCYANIDES.

Fractional precipitation of rare earth ferrocyanides ($KR[Fe(CN)_6].nH_2O$) has been recognized as an efficient method for the separation of erbium-yttrium mixtures. However, this method has been little used because the ferrocyanide precipitates have been difficult to prepare in a filterable form. Prandtl[3] was able to prepare filterable ferrocyanide precipitates by precipitation with potassium ferrocyanide from rare earth nitrate solutions containing nitric acid. However, the required nitric acid concentration results in oxidation of the ferrocyanide giving a gelatinous blue precipitate which nullifies the effects of crystallinity in the precipitate.

It was found that hydrochloric acid solutions were more desirable because there was no oxidation of the ferrocyanide. Erbium-yttrium mixtures were fractionated by adding twenty per cent potassium ferrocyanide solutions to the rare earth chloride solutions (two per cent rare earth oxide) in 3 *N* hydrochloric acid. The addition of five grams of ammonium chloride per gram of rare earth oxide to the rare earth solution promoted the formation of filterable precipitates.

Iron-free rare earths were recovered from the precipitates by converting them to hydroxides with fifty per cent sodium hydroxide solutions, igniting the hydroxides to oxides, and precipitating rare earth oxalates from chloride solutions of the oxides. The ferrocyanide mother liquors gave iron-free oxides after two oxalate precipitations and ignitions. The complete removal of iron is necessary for successful ferrocyanide precipitation.

Fractionation was followed by spectrophotometric analyses[1] for erbium, and fractions were combined according to their analyses.

The fractionations showed that ferrocyanide precipitation is the most rapid method available for the separation of yttrium from erbium.

V. SEPARATION OF YTTERBIUM AND THE PURIFICATION OF THULIUM AND LUTECIUM BY THE EXTRACTION OF YTTERBIUM WITH SODIUM AMALGAM.

The most important advance in the separation of the yttrium earths in recent years is the development of the amalgamation method for the separation of ytterbium. Marsh[4] has shown that ytterbium is the only ytterium earth element capable of forming an amalgam when acid yttrium earth acetate solutions are shaken with dilute liquid sodium amalgam. This makes possible the purification of ytterbium and the separation of ytterbium from its accompanying rare earths. Experiments were performed which verified the success reported by Marsh for this separation of ytterbium and which extended the applicability of the method.

Ytterbium was extracted from dilute solutions (0.3 per cent ytterbium oxide) of the perchlorate, chloride, formate, acetate, and alkaline citrate with 0.1 per cent sodium amalgam for various lengths of time. The degree of extraction was greatest with perchlorate, chloride and formate solutions, and least with alkaline citrate solutions. This indicated that when ytterbium is extracted from dilute solutions, salts of strong acids or non-coordinating anions must be used for most efficient extraction.

Extractions of ytterbium from natural rare earth mixtures in more concentrated solutions were successful with acetate and formate solutions. Chloride and perchlorate solutions were un-

satisfactory due to the formation of a stable sludge of mercury. Acetate solutions were preferable to formate solutions, and extraction from solutions at 50° was more efficient than extraction at room temperature. Extraction from acetate solutions was best at $pH = 5 — 5.5$.

Ytterbium-thulium and ytterbium-lutecium oxide mixtures were converted to acetate solutions. These solutions were repeatedly treated with 0.1 - 0.8 per cent sodium amalgam until traces of ytterbium remained in the aqueous solutions. From the initial oxides containing thirty-six to eighty-seven per cent ytterbium oxide[1], residues were obtained after extraction which gave oxides containing less than 0.2 - 6 per cent ytterbium oxide. The amount of ytterbium in the residues depended upon the number of extractions with sodium amalgam. Five to eleven extractions gave oxides containing less than 0.3 per cent ytterbium oxide. In this manner, lutecium and thulium oxides containing small amounts of ytterbium were prepared.

Sodium salts resulting from the extractions were separated from the rare earths by oxalate precipitation followed by precipitation of rare earth succinates from neutral nitrate solutions with ammonium succinate.

When ytterbium amalgam is decomposed by shaking with dilute acids, ytterbium passes into the aqueous solution as ytterbous ions. The hydrated ytterbous ion is green, and this green color can be utilized as a qualitative test for ytterbium. By adding sodium amalgam to aqueous chloride solutions and then decomposing the amalgam by adding hydrochloric acid, a green color is visible if ytterbium is present. The limit of detection is 0.002 g. of ytterbium. None of the other yttrium earths interfere with the test.

VI. PROPOSED PROCEDURE FOR THE SEPARATION OF THE YTTRIUM EARTHS.

Starting with a crude mixture of rare earths, the initial separation would consist of fractional precipitation of double rare earth sulfates until the yttrium earth fractions were free from cerium earths and contained relatively small amounts of the terbium earths. The yttrium earth fractions should be subjected

to bromate crystallization until mixtures consisting of yttrium-holmium, yttrium-erbium, and yttrium-erbium-thulium-ytterbium-lutecium are obtained.

The yttrium-holmium and ytterium-erbium mixtures can be separated most easily by fractional precipitation of the ferrocyanides, although a preliminary basicity separation may be necessary to remove part of the yttrium.

The yttrium-erbium-thulium-ytterbium-lutecium fractions could be most easily resolved into binary mixtures by using ytterbium as a "separating element." The addition of ytterbium to such a bromate crystallization would aid in giving ytterbium-thulium and ytterbium-lutecium mixtures. These binary mixtures can then be resolved by extracting ytterbium with sodium amalgam.

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Vita

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